

## Electron Transfer Catalysis in the Conversion of $\text{Fe}_3(\text{CO})_{12}$ to $\text{Fe}(\text{CO})_5$

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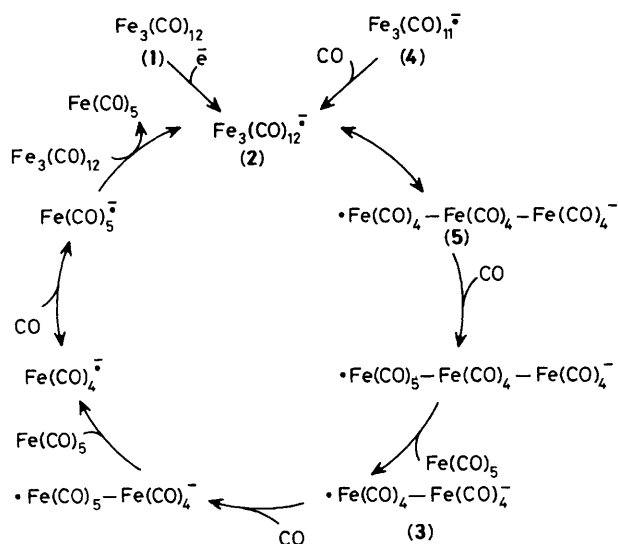
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Evidence strongly suggests that the reaction of  $\text{Fe}_3(\text{CO})_{12}$  with CO to yield  $\text{Fe}(\text{CO})_5$  occurs *via* an electron transfer catalysed pathway; a mechanism for the reaction is proposed.

Rapid ligand substitutions *via* an electron transfer chain mechanism have been observed in a vast number of organo-metallic systems.<sup>1</sup> The key steps which make the substitution possible are the formation of 17 and 19-electron intermediates leading to the labilisation of metal–ligand bonds. In this paper, we report a new application of this electron transfer catalysis in the metal–metal bond cleavage of  $\text{Fe}_3(\text{CO})_{12}$  (**1**) resulting in the degradation of the cluster to form a mononuclear species.

Complex (**1**) [ $1.0 \times 10^{-2}$  M in tetrahydrofuran (THF)] was

converted to  $\text{Fe}(\text{CO})_5$  in the presence of CO gas (1 atm), at ambient temperature, with an induction period of *ca.* 4 h. No reaction of (**1**) to  $\text{Fe}(\text{CO})_5$  occurred during the induction period; however, after this time complete conversion to  $\text{Fe}(\text{CO})_5$ , seen by the disappearance of the characteristic green colour of (**1**), required less than 15 min. Addition of 1% (v/v) of dimethylformamide (DMF), dimethyl sulphoxide (DMSO) or 0.01 equiv. of 2,2'-bipyridine to the THF solution reduced the induction period to *ca.* 1 h. In all cases,



Scheme 1

quantitative yields of  $\text{Fe}(\text{CO})_5$  were observed.<sup>†</sup> In the absence of excess of CO, (1) slowly decomposes in THF to yield 1.6 mol of  $\text{Fe}(\text{CO})_5$  and 0.080 mol of  $\text{HFe}_3(\text{CO})_{11}^-$  per mole of (1).<sup>‡</sup>  $\text{Fe}(\text{CO})_5$  was separated from  $\text{HFe}_3(\text{CO})_{11}^-$  by vacuum distillation. Complex (1) decomposed even faster in acetonitrile, DMF, and DMSO to yield  $\text{Fe}(\text{CO})_5$  and  $\text{HFe}_3(\text{CO})_{11}^-$ . The time needed for the decomposition is <5 min in DMF or DMSO, ca. 3 h in acetonitrile, and ca. 5 h in THF. Surprisingly, (1) is stable in n-pentane with <1% decomposition during 24 h at ambient temperature.

Results indicate that the decomposition of (1) and its reaction with CO are closely related to the presence of radical species. In THF, the reaction is inhibited by electron acceptors such as nitrobenzene and quinone. Moreover, 'aged' THF was found to increase the induction period to 2 days. The reacting solutions of (1) display three e.s.r. signals in variable relative intensities. These signals ( $g$  2.0014, 2.0387, and 2.0496) had been observed previously<sup>3,4</sup> and were conclusively assigned as  $\text{Fe}_3(\text{CO})_{12}^-$  (2),  $\text{Fe}_2(\text{CO})_8^-$  (3), and  $\text{Fe}_3(\text{CO})_{11}^-$  (4) respectively.<sup>4</sup> In general, the solutions which produced strong signals due to (2) and (3) resulted in fast formation of  $\text{Fe}(\text{CO})_5$ . In agreement with this observation, no e.s.r. signal was detected in n-pentane. An example of the e.s.r. spectral changes in DMF during the course of decomposition of (1) is shown in Figure 1. As displayed in the spectra, only (2) and (3) are present in the solutions in the first 2 minutes at 0°C. The peak assigned to (2) was found to increase and then decrease in intensity at a fast rate, while peak (3) was gradually replaced by peak (4), assigned to the radical anion  $\text{Fe}_3(\text{CO})_{11}^-$ . Different relative concentrations of (3) and (4) were observed for different solvents and temperatures, and it appears that the ratio is mainly controlled by the CO pressure in the system. Under one atmosphere of CO, (4) is completely converted to (3) indicating that reaction (1) had taken place. The observed paramagnetic species are likely to have been produced from the known disproportionation reaction of (1)<sup>5</sup> with electron

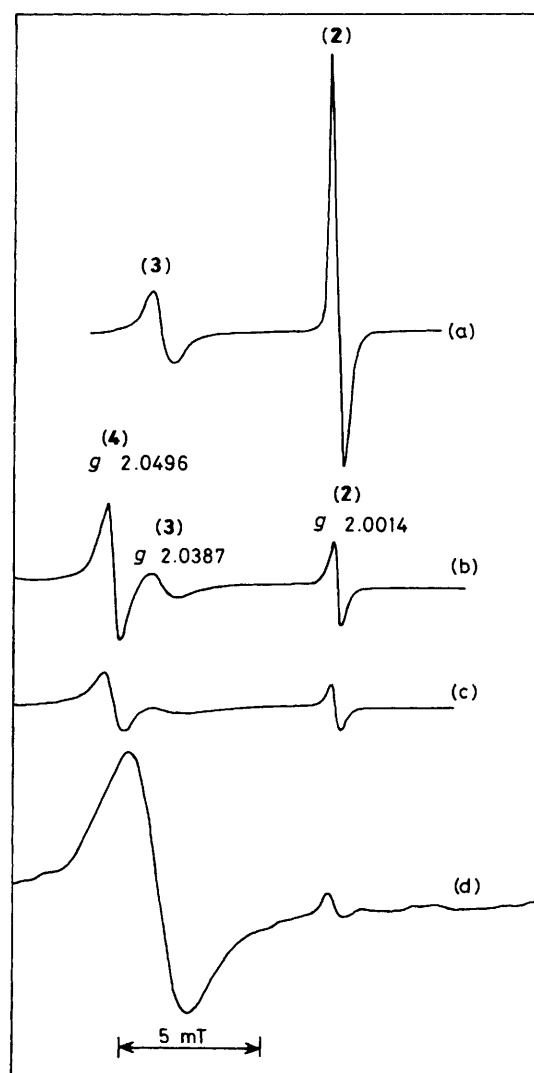
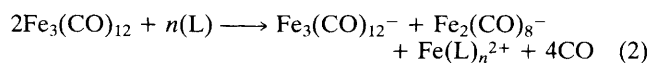
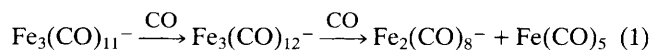


Figure 1. The e.s.r. signals observed when  $\text{Fe}_3(\text{CO})_{12}$  is dissolved in DMF. (a) Ca. 2 min after mixing at 0°C. (b) 20 min after mixing at 0°C. (c) Ca. 2 min after warming to 25°C. (d) 10 min after the introduction of CO (1 atm) into the e.s.r. tube followed by vigorous shaking.

donating solvent molecules or ligands as shown in equation (2). Difference in the length of induction period of the decomposition of  $\text{Fe}_3(\text{CO})_{12}$ , which varies for the solvents THF, acetonitrile, DMF and DMSO, presumably is the consequence of different reactivity of these solvents toward (1).



L = solvent molecule

The foregoing results suggest that the conversion of  $\text{Fe}_3(\text{CO})_{12}$  to  $\text{Fe}(\text{CO})_5$  in solution proceeds *via* an electron transfer catalysed process. A detailed mechanism proposed to

<sup>†</sup> The amounts of  $\text{Fe}(\text{CO})_5$  and  $\text{HFe}_3(\text{CO})_{11}^-$  were determined spectrophotometrically by comparison of the i.r. CO absorptions with authentic samples.

account for the catalysis is shown in Scheme 1, involving the reactions of CO with a series of iron radical anions, 17; 18, and 19-electron species. One of the key steps in this scheme is the reversible ring opening of the 19-electron triangular radical (**2**) to give the 17-electron linear chain radical (**5**). This step may be rationalized on the basis of results of a previous MO calculation which indicated that the LUMO of (**1**) possesses strong metal-metal anti-bonding character.<sup>7</sup> In the last step of the cycle, the extra electron in  $\text{Fe}(\text{CO})_5^-$  is transferred to  $\text{Fe}_3(\text{CO})_{12}$  regenerating (**2**). This mechanism is further supported by the observation that the addition of benzophenone radical anion (0.0100 M; 1 ml) to (**1**) (0.100 M; 10.0 ml) in THF in the presence of CO (1 atm) leads to a complete conversion of the iron cluster to  $\text{Fe}(\text{CO})_5$  within 15 min. This observation indicates that each electron transferred from the benzophenone radical anion to (**1**) leads to the formation of 300 molecules of  $\text{Fe}(\text{CO})_5$ .

This mechanism provides a new pathway for metal cluster degradation.

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